2002-239972

[Document Name] Application for Patent
[Reference No.] 30595
[Application Date] August 20, 2002 (Heisei 14)
[Addressee] Commissioner, Patent Office
[International Patent Classification] G11B 7/24
C22C 5/08
C23C 14/06
C23C 14/14
[Title of the Invention] REFLECTIVE FILM AND SEMI-TRANSMISSIVE REFLECTIVE FILM FOR OPTICAL INFORMATION RECORDING MEDIUM, AND OPTICAL INFORMATION RECORDING MEDIUM, AND SPUTTERING TARGET FOR OPTICAL INFORMATION RECORDING MEDIUM
[Number of Claim(s)] 8

[Inventor]
[Address] c/o Kobe Corporate Research Laboratories in Kobe Steel, Ltd. 5-5, Takatsukadai 1-chome, Nishi-ku, Kobe-shi, Hyogo 651-2271 Japan
[Name] Yuuki TAUCHI
[Inventor]
[Address] c/o Kobe Corporate Research Laboratories in Kobe Steel, Ltd. 5-5, Takatsukadai 1-chome, Nishi-ku, Kobe-shi, Hyogo 651-2271 Japan
[Name] Junichi NAKAI
[Inventor]
[Address] c/o Kobe Corporate Research Laboratories in Kobe Steel, Ltd. 5-5, Takatsukadai 1-chome, Nishi-ku, Kobe-shi, Hyogo 651-2271 Japan
[Name] Katsutoshi TAKAGI

[Applicant]

[Identification No.] 000001199

[Name] Kabushiki Kaisha Kobe Seikosyo

(Kobe Steel, Ltd.)

[Agent]

[Identification No.] 100067828

[Patent Attorney]

[Name] Etsuji KOTANI

[Appointed Agent]

[Identification No.] 100075409

[Patent Attorney]

[Name] Kyuichi UEKI

[Indication of Fee]

[Deposit Account No.] 012472

[Amount of Payment] ¥21,000

[List of Accompanying Document]

[Name of Document] Specification 1

[Name of Document] Abstract 1

[No. of General Power of Attorney] 9703961

[Requirements of Proofreading] Required

[Name of the Document] SPECIFICATION

[Title of the Invention] REFLECTIVE FILM AND SEMI-TRANSMISSIVE REFLECTIVE FILM FOR OPTICAL INFORMATION RECORDING MEDIUM, AND OPTICAL INFORMATION RECORDING MEDIUM, AND SPUTTERING TARGET FOR OPTICAL INFORMATION RECORDING MEDIUM

[Claims]

[Claim 1] An Ag base alloy reflective film or semi-transmissive reflective film for optical information recording medium characterized by being an Ag base alloy containing Bi and/or Sb in a total amount of 0.005 to 0.4 % (below, denoting atomic %, unless otherwise specified).

[Claim 2] The Ag base alloy reflective film or semi-transmissive reflective film for optical information recording medium according to claim 1, wherein the Ag base alloy contains at least one of rare earth metal elements.

[Claim 3] The Ag base alloy reflective film or semi-transmissive reflective film for optical information recording medium according to claim 2, wherein the rare earth metal elements are Nd and/or Y.

[Claim 4] The Ag base alloy reflective film or semi-transmissive reflective film for optical information recording medium according to claim 3, comprising Nd and/or Y as the rare earth metal elements in a total amount of 0.1 to 2 %.

[Claim 5] The Ag base alloy reflective film or semi-transmissive reflective film for optical information recording medium according to any of claims 1 to 4, wherein the Ag base alloy contains at least one selected from Cu, Au, Rh, Pd, and Pt in a total amount of 0.1 to 3 %.

[Claim 6] An Ag base alloy sputtering target for optical information recording medium characterized by being composed of the Ag base alloy according to any of claims 1 to 5.

[Claim 7] An optical information recording medium characterized by including the Ag base alloy reflective film according to any of claims 1 to 5.

[Claim 8] An optical information recording medium characterized by including the Ag base alloy semi-transmissive reflective film according to any of claims 1 to 5.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Pertains]

The present invention relates to a reflective film or a semi-transmissive reflective film for an optical information recording medium having high thermal conductivity / high reflectance / high durability, and a sputtering target for an optical information recording medium to be used for deposition of the reflective film or the semi-transmissive reflective film, and an optical information recording medium having the reflective film or the semi-transmissive reflective film in the

field of optical information recording media such as CD (Compact Disc) and DVD (Digital Versatile Disc).

[0002]

[Prior Art]

Optical information recording media (optical disks) include some types, and fall roughly into 3 types of (1) read-only, (2) write-once, and (3) writable, based on the recording and reproduction system.

[0003]

First, the read-only optical disk of (1) has a structure in which a reflective film (metal film) containing Al, Ag, Au, or the like as a main component is stacked on a transparent plastic (e.g., polycarbonate) substrate including pits of unevenness (recorded data) formed thereon. It performs the reproduction of the recorded data by detecting the reflectance difference and the phase difference of a laser light applied onto the optical disk. Such optical disks include a single side single layer type made of a transparent plastic substrate including a reflective film deposited thereon, a single side dual layer type which has been doubled in recording capacity by bonding a transparent plastic substrate including a reflective film deposited thereon and the one including a semi-transmissive reflective film deposited thereon to each other by an adhesive, and other types. As the optical disks adopting such systems, mention may be made of CD-ROM, DVD-ROM,

and the like.

[0004]

Then, the write-once optical disk of (2) has a structure in which a recording film (organic dye film) and a reflective film (metal film) are stacked on a transparent plastic substrate. With the optical disk, the recording film is allowed to generate heat / is decomposed by laser light irradiation, so that grooves (guiding grooves previously cut in the substrate) are deformed. Thus, data is recorded. By detecting the difference between the reflectance of the decomposed portion and the reflectance of the non-decomposed portion of the recording film by a laser light, the reproduction of data is performed. This optical disk is characterized in that once recorded data is unrewritable (only one recording and repeatable reproduction), and examples of the optical disk adopting such a system may include CD-R, DVD-R, and DVD+R.

[0005]

Whereas, the writable optical disk of (3) has, as a basic structure, a structure in which dielectric protective film / recording film / dielectric protective film / reflective film (metal film) are stacked on a transparent plastic substrate. It records data by utilizing the reversible phase change between crystalline-non-crystalline phase of the recording film caused by laser light irradiation. The reproduction of the recorded data is performed by detecting the difference in reflectance

between the crystalline portion and the non-crystalline portion of the recording film. The optical disk is characterized by rewritability of data one thousand times to one hundred thousand times (repeatable recording and reproduction). Examples of the optical disk of such a system may include CD-RW, DVD-RAM, DVD-RW, and DVD+RW.

[0006]

For the reflective films or the semi-transmissive reflective films included in the foregoing optical disks of (1) to (3), Au, Al, Ag, or alloys containing these as main components have been widely used from the viewpoints of thermal conductivity, reflectance, and durability.

[0007]

Out of these, the Au-based reflective film containing Au as a main component is excellent in durabilities (chemical stability and thermal stability), and hence the recording reproducing characteristics of the optical disk are resistant to deterioration with time. However, the raw material cost is high, and further, the required high reflectance is unfavorably difficult to obtain for a violet laser (wavelength: 405 nm) to be used for a next-generation optical disk (Blu-ray Disc, or the like).

[0008]

The Al-based reflective film containing Al as a main component has the following features: it requires a low raw

material cost, which allows the cost reduction of an optical disk; and further, it can provide a high reflectance for a violet laser to be used for a next-generation optical disk. However, it has a lower durability than that of the Au-based reflective film. Further, unfavorably, it cannot acquire a high heat conductivity for exhibiting a function as a thermal heat diffusion film required when used as a reflective film of a write-once / writable optical disk.

[0009]

The Ag-based reflective film containing Ag as a main component has the following features: it has high reflectance with respect to a violet laser for use in a next-generation optical disk, and high thermal conductivity required of a write-once / writable disk; and, in addition, the raw material cost thereof is lower as compared with an Au-based reflective film. Therefore, it is a promising material as a reflective film or a semi-transmissive reflective film. However, it is superior to an Al-based reflective film in terms of durability, but it does not have durability as high as that of the Au-based reflective film. In order to put it into actual use as a reflective film or a semi-transmissive reflective film of an optical disk, it is necessary to improve the durability without impairing the high reflectance and the high thermal conductivity inherently possessed by Ag.

[0010]

As for the means for improving the durability of such an Ag-based reflective film, the following improvement measures have been reported. For example, the durability (chemical stability) is respectively improved by adding Au, Pd, Cu, Rh, Ru, Os, Ir, and Pt to Ag in U.S. Pat. No. 6,007,889, or by adding Pd and Cu to Ag in JP-A No. 208732/1994. Further, the present inventors also have proposed a method in which the durability (thermal stability in the inhibition of grain growth, or the like) is improved by adding rare earth metal elements to Ag in JP-A 15464/2002.

[0011]

However, for high-speed recording DVDs or next-generation optical disks, the levels of characteristics required of the reflective film have been further raised. This results in demands for durability, thermal conductivity, and reflectance of higher levels than ever before.

[0012]

Particularly, for the durability, there is a demand for high corrosion resistance against halogen elements including chlorine. This demand is particularly prominent for a write-once optical disk in which a halogen element-containing organic dye recording film, a protective film, an adhesive layer, and the like are directly stacked on a reflective film. Further, as distinct from a DVD, the next-generation optical disk is in an inverted stacked configuration obtained in the following

manner. First, a reflective film is deposited on a transparent plastic substrate, and dielectric protective film / recording film / dielectric protective film / are stacked and deposited thereon. For this reason, the surface roughness of the reflective film must be extremely reduced in order to suppress the deterioration of the recording and reproduction characteristics. Further, the next-generation optical disk is required to be capable of keeping the stability of the surface roughness even when put under a thermal load.

[0013]

Whereas, as for the thermal conductivity, the heat generated in the very small region of the recording film through laser light irradiation is required to be rapidly diffused. Thus, in order for the reflective film to also have the function as a thermal diffusion film, the film is required to have high thermal conductivity.

[0014]

Further, as for the reflectance, the reflective film is required to have high reflectance also with respect to the violet laser for use in a high-speed DVD or a next-generation optical disk.

[0015]

However, no Ag base alloy has been yet found which satisfies all these requirements. In order that the reflective film may ensure high reliability as being used for a high-speed

DVD or a next-generation optical disk, there is a strong demand for an Ag base alloy which has all the required characteristics of high thermal conductivity, high reflectance, and high durability.

[0016]

[Problems to be Solved by the Invention]

In view of the foregoing circumstances, the present invention has been completed. It is an object thereof to provide an Ag base alloy reflective film or semi-transmissive reflective film for an optical information recording medium having high reliability as being used for a high-speed DVD or a next-generation optical disk, and an Ag base alloy sputtering target for an optical information recording medium to be used for the deposition of the reflective film or the semi-transmissive reflective film, and an optical information recording medium including the reflective film or the semi-transmissive reflective film by finding an Ag base alloy having higher thermal conductivity / higher reflectance / higher durability than those of pure Ag or conventional Ag alloys.

[0017]

[Means for Solving the Problems]

The gist of a reflective film or semi-transmissive reflective film for an optical information recording medium (optical disk) in accordance with the present invention, which

could solve the foregoing problem, resides in that it is made up of an Ag base alloy containing Bi and/or Sb in a total amount of 0.005 to 0.4 % (below, denoting atomic %, unless otherwise specified). The reflective film and the semi-transmissive reflective film which are the Ag base alloys of such a composition have all of high thermal conductivity / high reflectance, and high durability.

[0018]

As the Ag base alloy, more preferred is the one containing at least one of rare earth metal elements. The one containing Nd and/or Y as the rare earth metal elements is preferred because it exhibits ever more excellent durabilities (particularly, thermal stability). Incidentally, Nd and/or Y is preferably contained in a total amount of 0.1 to 2 %.

[0019]

Further, it is also effective that the Ag base alloy is allowed to contain at least one selected from Cu, Au, Rh, Pd, and Pt. If these elements are contained in a total amount of 0.1 to 3 %, it is possible to suppress the changes in appearance due to high durabilities, particularly, excellent chemical stability, and to keep the high reflectance.

[0020]

Incidentally, the present invention also covers an Ag base alloy sputtering target for an optical information recording medium composed of the foregoing Ag base alloy.

[0021]

Further, an optical information recording medium having a reflective film or a semi-transmissive reflective film made of the Ag base alloy is also one of the preferred embodiments of the present invention.

[0022]

[Mode for Carrying Out the Invention]

The present inventors have conducted a close study under the foregoing problems in order to provide an Ag base alloy reflective film or semi-transmissive reflective film for an optical information recording medium having high thermal conductivity, high reflectance, and high durability. As a result, they found that an Ag base alloy containing Bi and/or Sb in a total amount of 0.005 to 0.4 % has high reflectance and high thermal conductivity comparable to those of pure Ag, and is capable of exhibiting a higher level of durability than that of pure Ag, leading to the completion of the present invention. Below, the present invention will be described in details.

[0023]

An Ag base alloy reflective film or semi-transmissive reflective film for an optical information recording medium of the present invention comprises an Ag base alloy containing Bi and/or Sb in a total amount of 0.005 to 0.4 % as an essential element. Such a reflective film or a semi-transmissive reflective film comprising the Ag base alloy not only has high

thermal conductivity and high reflectance comparable to those of pure Ag, but also has excellent durabilities (thermal stability and chemical stability).

[0024]

In general, a pure Ag thin film deposited by a sputtering process or the like includes a large number of crystal defects (such as void, dislocation, and grain boundary). Ag atoms are readily diffused through the crystal defects. Therefore, when a pure Ag thin film is held under a high temperature high humidity environment, Ag atoms are diffused / aggregated at various sites, resulting in increases in surface roughness and crystal grain size. Whereas, also when put under an environment containing halogen ions such as chlorine ions, similarly, Ag atoms are readily diffused / aggregated. The changes in thin film surface caused by such an aggregation entails a reduction in reflectance, which remarkably deteriorates the recording and reproduction characteristics of an optical disk. In particular, with a very thin semi-transmissive reflective film used for a DVD-ROM, the effect of aggregation exerted on the reflectance is large, so that the reproduction characteristics of an optical disk are remarkably deteriorated.

[0025]

As the solving measures for the foregoing problems, alloying of Ag has been studied so far. For example, alloying through the addition of a noble metal element (such as Au, Pd,

or Pt) to Ag, or through the addition of a rare earth metal element (such as Y), has been proposed.

[0026]

However, if a noble metal element (such as Au, Pd, or Pt) is added to Ag for alloying, the aggregation of Ag atoms due to the effects of chlorine ions, or the like is suppressed, but it is not possible to suppress the aggregation of Ag atoms due to holding under high temperatures and high humidities. Whereas, with a method in which a rare earth metal element (such as Y) is added for alloying, the aggregation of Ag atoms due to holding under high temperatures and high humidities is suppressed. However, it is not possible to suppress the aggregation of Ag atoms due to the effects of chlorine ions or the like. Namely, even with alloying using either of the element groups, it is not possible to simultaneously suppress the aggregations of Ag atoms resulting from both of holding under high temperatures and high humidities and the effects of chlorine ions.

[0027]

However, with the present inventors, by adopting an Ag base alloy containing Bi and/or Sb in a total amount of 0.005 % or more, it is possible to simultaneously suppress the aggregations of Ag atoms due to holding under high temperatures and high humidities and the effects of chlorine ions. Further, it has been shown that these elements exhibit a more clear

aggregation suppression effect with an increase in its content. However, the addition of such an element to Ag tends to reduce the thermal conductivity and the reflectance relative to the pure Ag thin film. This tendency becomes more noticeable with an increase in content of the element. This results in reductions in the thermal conductivity and the reflectance of the Ag base alloy thin film.

[0028]

As for the content of the elements, the upper limit of the total content can be raised up to 3 % from the viewpoint of ensuring high reflectance with respect to a violet laser for use in a next-generation optical disk. However, if the total content exceeds 0.4 %, it becomes impossible to ensure high thermal conductivity required of the reflective film of a high-speed DVD or a next-generation optical disk. Therefore, the upper limit of the total content has been set at 0.4 % as the requirement for ensuring both the characteristics of high reflectance and high thermal conductivity. On the other hand, if the total content is less than 0.005 %, the aggregation suppression effect through the addition of Bi and/or Sb is not effectively exhibited. It is preferably 0.01 % or more and 0.3 % or less, and more preferably 0.05 % or more and 0.2 % or less.

[0029]

Incidentally, in the present invention, for the purpose of further improving the durability, particularly the thermal

stability of an Ag base alloy containing Bi and/or Sb, it is also effective to add rare earth metal elements other than the foregoing elements. These elements have effects of further suppressing the aggregation of Ag atoms due to holding under high temperatures and high humidities, and still further enhancing the durability. As the rare earth metal element, Nd and/or Y is preferred. The amount of these elements added based on the amount of the Ag base alloy is preferably set at 0.1 % or more and 2 % or less in a total amount of Nd and/or Y. This is for the following reason: if the amount is less than 0.1 %, effective effects through the addition of the elements cannot be produced, and if the element is added in an amount in excess of 2 %, high thermal conductivity cannot be obtained. The amount is preferably 0.1 % or more and 1 % or less, and more preferably 0.1 % or more and 0.5 % or less.

[0030]

Further, at least one selected from Cu, Au, Rh, Pd, and Pt may also be added for the purpose of improving the durability, particularly the chemical stability of the Ag base alloy containing Bi and/or Sb. These elements have effects of further suppressing the aggregation of Ag atoms due to the effects of chlorine ions, and still further enhancing the durability. In order for the aggregation suppression effect of Ag atoms to be effectively exhibited, the total amount added is set at preferably 0.1 % or more and 3 % or less. It is more preferably

0.1 % or more and 2 % or less.

[0031]

Whereas, in order to attain the further improvement of the chemical stability of the Ag base alloy, it is also effective to add Mg, Ti, and Zn in addition to the foregoing elements. The addition of these elements produces a lower durability improvement effect than with Au, Rh, Pd, and Pt. However, it is useful for achieving a cost reduction of an optical disk because of its low raw material cost. Incidentally, Mg, Ti, and Zn reduce the thermal conductivity and the reflectance with an increase in amount thereof. Therefore, the upper limit of the total amount of these elements added is set at 3 %. Incidentally, as for the foregoing alloy element group, even addition of one kind can produce a sufficient effect. However, it is needless to say that it is possible to produce the same effect even for the addition of two or more kinds in combination. However, the foregoing effects obtainable through the addition of Nd and/or Y as a rare earth metal element, and the foregoing effects obtainable through the addition of at least one selected from Cu, Au, Rh, Pd, and Pt are the inherent effects observable for the Ag base alloy containing Bi and/or Sb. For example, the same effects are not observable with pure Ag.

[0032]

Incidentally, as also disclosed in, for example, JP-A No. 184725/2001, there is known an Ag alloy which has been improved

in corrosion resistance by adding at least one element selected from Al, Au, Cu, Co, Ni, Ti, V, Mo, Mn, Pt, Si, Nb, Fe, Ta, Hf, Ga, Pd, Bi In, W, and Zr in an amount of 0.5 to 5 % to Ag. However, Al, Au, Cu, Pt, and Pd do not have an effect of suppressing the aggregation of Ag atoms occurring when the Ag film has been held at high temperatures. As a result, it is not possible to obtain the durability improvement effect from the viewpoint of the thermal stability mentioned as the object in the present invention. Whereas, addition of Bi in an amount of 0.5 % or more reduces the thermal conductivity, and hence it is not preferred, and excluded from the present invention. Further, in JP-A No. 92959/2002, there is disclosed an Ag alloy which has been improved in chemical stability by adding Cu in an amount of 4 to 15 mass%, and Al, Zn, Cd, Sn, Sb, and Ir in an amount of 0.5 mass% or more to Ag. However, Cu, Al, Zn, Cd, Sn, and Ir do not produce an effect of suppressing the aggregation of Ag atoms due to holding under high temperatures. Whereas, addition of Sb in an amount of 0.5 mass% (0.44 %) or more reduces the thermal conductivity inherent in Ag, and hence it is not preferred. Therefore, these known Ag alloys are distinctly distinguished from the present invention in terms of the specific constitution and functional effects.

[0033]

The Ag base alloy reflective film and the Ag base alloy semi-transmissive reflective film for optical information

recording media of the present invention can be obtained by depositing the Ag base alloy of the foregoing alloy composition on a substrate with a vacuum deposition process, an ion plating process, a sputtering process, or the like. Out of these, the one deposited by a sputtering process is recommendable. This is for the following reason. The Ag base alloy reflective film and the Ag base alloy semi-transmissive reflective film deposited by a sputtering process are superior in alloy element distribution and the in-plane uniformity of the film thickness to the films deposited by other deposition process. As a result, the film is favorably exploited to show higher level of characteristics (high thermal conductivity, high reflectance, and high durability) as a reflective film, which allows the production of high-performance high-reliability optical disk.

[0034]

Incidentally, the Ag base alloy reflective film for an optical information recording medium in the present invention is a thin film for use as a reflective film for single-layer recording for performing recording only on one side of a disk, or the uppermost layer reflective film for multilayer recording. The transmittance is almost 0 %, and the reflectance is defined by the constitution of the disk, and about 45 % or more. Whereas, the film thickness may be appropriately determined in such a range as to meet the foregoing reflectance and transmittance, and it may be normally set at about 50 to 200 nm.

[0035]

Whereas, the semi-transmissive reflective film of the present invention is a film for use as a reflective film of a medium for performing two or more multilayer recording on one side of a disk. The transmittance / reflectance are defined according to the configuration of the disk. However, the semi-transmissive reflective film denotes a thin film having a transmittance of about 60 to 72 % and a reflectance of about 18 to 30 %. Further, the thickness thereof may be appropriately determined in such a range as to meet the foregoing reflection and transmittance requirements, and it may be normally set at about 5 to 20 nm.

[0036]

The Ag base alloy sputtering target for an optical information recording medium of the present invention can be manufactured by any method of a dissolution / casting process, a powder sintering process, a spray forming process, and other processes. Out of these, manufacturing by a vacuum dissolution / casting process is recommendable. This is for the following reason. The Ag base alloy sputtering target manufactured by the vacuum dissolution / casting process has a lower content of impurity components such as nitrogen and oxygen than that of the one manufactured by other process. As a result, the reflective film or the semi-transmissive reflective film deposited by using the sputtering target is effectively

exploited to show high characteristics (high thermal conductivity, high reflectance, and high durability) as a reflective film, which allows the production of high-performance high-reliability optical disk.

[0037]

The optical information recording medium of the present invention may include the Ag base alloy reflective film or semi-transmissive reflective film of the present invention. There is no other particular restriction on the constitution as the optical information recording medium. In the optical information recording medium field, all known constitutions are adoptable. For example, the optical information recording medium of the present invention including the reflective film or semi-transmissive reflective film made of the foregoing Ag base alloy on one side of a transparent substrate of polycarbonate or the like has high reflectance, high thermal conductivity, and high durability. Therefore, as a matter of course, it can be used as a read-only, writing once, writable, or other type of optical information recording medium, as well as it can also be preferably used for a high-speed DVD or a next-generation optical disk.

[0038]

[Examples]

Below, the present invention will be described in more details by way of experimental examples. However, the

following experimental examples should not be construed as limiting the scope of the invention. All of modifications or changes practiced within a scope not departing from the spirit of the present invention are included in the technical range of the present invention. Incidentally, respective characteristics were measured or evaluated in the following manner.

[0039]

[Manufacturing of Ag base alloy thin film]

With a DC magnetron sputtering process, each thin film of pure Ag (sample No. 1), Ag-Bi alloys (sample Nos. 2 to 5), Ag-Sb alloys (sample Nos. 6-9), Ag-Bi-Nd alloys (sample Nos. 10 to 14), Ag-Bi-Y alloys (sample Nos. 15-19), Ag-Sb-Nd alloys (sample Nos. 20 to 24), Ag-Sb-Y alloys (sample Nos. 25 to 29), Ag-Bi-Cu alloys (sample Nos. 30 to 34), Ag-Bi-Au alloys (sample Nos. 35 to 39), Ag-Sb-Cu alloys (sample Nos. 40 to 44), Ag-Sb-Au alloys (sample Nos. 45 to 49), Ag-Bi-Nd-Cu alloy (sample No. 50), Ag-Bi-Nd-Au alloy (sample No. 51), Ag-Bi-Y-Cu alloy (sample No. 52), Ag-Bi-Y-Au alloy (sample No. 53), Ag-Sb-Nd-Cu alloy (sample No. 54), Ag-Sb-Nd-Au alloy (sample No. 55), Ag-Sb-Y-Cu alloy (sample No. 56), Ag-Sb-Y-Au alloy (sample No. 57), Ag-Si alloy (sample No. 58), and Ag-Sn alloy (sample No. 59), with a film thickness of 100 nm (as a reflective film), or 15 nm (as a semi-transmissive reflective film) was deposited on a polycarbonate substrate (diameter: 50 mm, thickness: 1 mm).

Then, each composition of these Ag base alloy thin films was examined by an ICP (inductively coupled plasma) emission spectrometric analysis method.

[0040]

Then, using each Ag base alloy thin film manufactured, the characteristics (thermal conductivity, reflectance, and durability) as a reflective film (film thickness 100 nm) or a semi-transmissive reflective film (15 nm) were examined. In particular, as for the thermal stability out of the durabilities, the changes in reflectance before and after a high-temperature high-humidity test, surface roughness (average roughness), crystal grain diameter, and the like were examined. As for the chemical stability out of the durabilities, the changes in appearance after a salt immersion test were examined. Thus, the durabilities of each thin film were evaluated.

[0041]

Example 1 [Measurement of thermal conductivity]

The thermal conductivity of each thin film with a thickness of 100 nm manufactured as described above was measured in the following manner. The sheet resistance Rs was measured with a four probe method by means of 3226-mΩ Hi TESTER manufactured by HIOKI Co, and the film thickness t was measured by means of alpha-step 250 manufactured by TENCOR INSTRUMENTS Co. Then, the electrical resistivity ρ (= sheet resistance Rs × film thickness t) was calculated, and then, the thermal

conductivity κ (= 2.51 × absolute temperature T / electrical resistivity ρ) at an absolute temperature of 300 K (≒ 27 °C) was calculated by the law of Wiedemann-Franz. Incidentally, for the evaluation, the one showing 256 W/(m·K) or more, which corresponds to 80 percent or more of the thermal conductivity: 320 W/(m·K) of a pure Ag thin film has been judged as having high thermal conductivity. The results are shown in Tables 1 and 2.

[0042]

As apparent from Tables 1 and 2, any of the pure Ag thin film (sample No. 1), the Ag-Si alloy (sample No. 58) thin film, and the Ag base alloy thin films of sample Nos. 2 to 4, 6 to 8, 10 to 13, 15 to 18, 20 to 23, 25 to 28, 30 to 33, 35 to 38, 40 to 43, 45 to 48, and 50 to 58, which satisfy the defined requirements of the present invention has high thermal conductivity. In contrast, for the Ag base alloy thin films of sample Nos. 5, 9, 14, 19, 24, 29, 34, 39, 44, and 49, it is not possible to obtain a prescribed high thermal conductivity because of the too large amount of the alloy elements to be added. Whereas, also for the thin film of the Ag-Sn alloy (sample No. 59), it is not possible to obtain high thermal conductivity. Incidentally, the addition effects of Rh, Pd, and Pt are the same as the addition effects of Cu or Au.

[0043]

[Table 1]

[0044]

[Table 2]

[0045]

Example 2 [Measurement of reflectance]

The reflectance with respect to a visible light (wavelength: 400 to 800 nm) of each thin Ag base alloy film with a thickness of 100 nm manufactured in the foregoing manner was measured by means of Polar Kerr Scope NEO ARK MODEL BH-810 manufactured by Nihon Kagaku Engineering Co. Incidentally, for the evaluation of high reflectance, the one showing 80 % or more (wavelength 405 nm) and 88 % or more (wavelength 650 nm) relative to 90.8 % (wavelength 405 nm) and 92.5 % (wavelength 650 nm), respectively, which are the reflectances of the pure Ag thin film has been judged as having a high reflectance. Herein, the wavelength of 405 nm is the wavelength of a laser light to be used for a next-generation optical disk, and the wavelength of 650 nm is the wavelength of a laser light to be used for a DVD. The results are shown in Tables 3 and 4.

[0046]

As apparent from Tables 3 and 4, any of the pure Ag thin film (sample No. 1), the thin films of the Ag-Si alloy (sample No. 58) and the Ag-Sn alloy (sample No. 59), and the Ag base alloy thin films of sample Nos. 2 to 4, 6 to 8, 10 to 13, 15

to 18, 20 to 23, 25 to 28, 30 to 33, 35 to 38, 40 to 43, 45 to 48, and 50 to 59, which satisfy the defined requirements of the present invention has high thermal conductivity. In contrast, for the Ag base alloy thin films of sample Nos. 5, 9, 14, 19, 24, 29, 34, 39, 44, and 49, it is not possible to obtain a prescribed high reflectance because of the too large amount of the alloy elements to be added. Incidentally, the addition effects of Rh, Pd, and Pt are the same as the addition effects of Cu or Au.

[0047]

[Table 3]

[0048]

[Table 4]

[0049]

Example 3 [Durability test 1: Evaluation of thermal stability]

Each of the same 100 nm-thick Ag base alloy thin films as those used for the measurement of the reflectance of Example 2 was subjected to a high-temperature high-humidity test (temperature 80 °C - humidity 90 % RH – retention time 48 hours). After the test, the reflectance was measured again. For the evaluation, the one showing absolute values of the changes in reflectance before and after the high-temperature

high-humidity test of 5 % or less (wavelength 405 nm) and 1 % or less (wavelength 650 nm) has been judged as having high durability. The results are shown in Tables 5 and 6.

[0050]

As apparent from Tables 5 and 6, any of the Ag base alloy thin films of the sample Nos. 2 to 57 satisfying the defined requirements of the present invention has high durability. In contrast, for the thin films of the pure Ag (sample No. 1), the Ag-Si alloy (sample No. 58), and the Ag-Sn alloy (sample No. 59), it is not possible to obtain a prescribed high durability. Incidentally, the addition effects of Rh, Pd, and Pt are the same as the addition effects of Cu or Au.

[0051]

[Table 5]

[0052]

[Table 6]

[0053]

Example 4 [Durability test 2: Evaluation of chemical stability]

Each of the 15 nm-thick Ag base alloy thin films manufactured in the foregoing manner was subjected to a salt immersion test (salt water concentration: 0.05 mol/l for NaCl, salt water temperature: 20 °C, immersion time: 5 minutes). The

changes in appearance of the thin film after the test were visually observed. For the evaluation, the one of which the changes in appearance such as discoloration and peeling were not observed has been judged as having high durability. The results are shown in Tables 7 and 8.

[0054]

As apparent from Tables 7 and 8, any of the Ag base alloy thin films of the sample Nos. 2 to 57 satisfying the defined requirements of the present invention has high durability. In contrast, for the thin films of the pure Ag (sample No. 1), the Ag-Si alloy (sample No. 58), and the Ag-Sn alloy (sample No. 59), it is not possible to obtain a prescribed high durability. Incidentally, the addition effects of Rh, Pd, and Pt are the same as the addition effects of Cu or Au.

[0055]

[Table 7]

[0056]

[Table 8]

[0057]

Example 5 [Durability test 3: Evaluation of thermal stability]

For each of the 100 nm-thick Ag base alloy thin films manufactured in the foregoing manner, the surface morphology observation and the surface roughness (average roughness: Ra) measurement were carried out by means of Nanoscope IIIa scanning

probe microscope manufactured by Digital Instruments Co., in AFM: atomic force microscope mode. Then, a high-temperature high-humidity test (temperature 80 °C - humidity 90 % RH - retention time 48 hours) was performed using each thin film subjected to the AFM measurement. After the test, the surface morphology observation and the surface roughness (average roughness: Ra) measurement were carried out again. For the evaluation, the one which showed a surface roughness of less than 1 nm both before and after the high-temperature high-humidity test have been judged as having high durability. The results are shown Tables 9 and 10.

[0058]

As apparent from Tables 9 and 10, any of the Ag base alloy thin films of the sample Nos. 2 to 57 satisfying the defined requirements of the present invention has high durability. In contrast, for the thin films of the pure Ag (sample No. 1), the Ag-Si alloy (sample No. 58), and the Ag-Sn alloy (sample No. 59), it is not possible to obtain a prescribed high durability. Incidentally, the addition effects of Rh, Pd, and Pt are the same as the addition effects of Cu or Au.

[0059]

[Table 9]

[0060]

[Table 10]

[0061]

As apparent from the results of Tables 1 to 10 shown above, the Ag base alloy thin films of the samples 2 to 4, 6 to 8, 10 to 13, 15 to 18, 20 to 23, 25 to 28, 30 to 33, 35 to 38, 40 to 43, 45 to 48, and 50 to 57, which satisfy the requirements of the present invention, have high performances in terms of all of high thermal conductivity, high reflectance, and high durability. In particular, the ones (sample Nos. 10 to 14) obtained by adding Nd as a rare earth metal element to the Ag-Bi alloy (sample No. 3), the ones (sample Nos. 15 to 19) obtained by adding Y thereto, or the ones (sample Nos. 30 to 34) obtained by adding Cu thereto, and the ones (sample Nos. 35 to 39) obtained by adding Au thereto have an improved durability as compared with the Ag-Bi alloy (sample No. 3). Similarly, the ones (sample Nos. 20 to 24) obtained by adding Nd as a rare earth metal element to the Ag-Sb alloy (sample No. 7), the ones (sample Nos. 25 to 29) obtained by adding Y thereto, or the ones (sample Nos. 40 to 44) obtained by adding Cu thereto, and the ones (sample Nos. 45 to 49) obtained by adding Au thereto have an improved durability as compared with the Ag-Sb alloy (sample No. 7). Further, the one (sample No. 50) obtained by adding both of Nd and Cu to the Ag-Bi alloy (sample No. 3), the one (sample No. 51) obtained by adding Nd and Au thereto, the one (sample No. 52) obtained by adding Y and Cu thereto, and the one (sample No. 53) obtained by adding Y and Au thereto have a still further improved durability as compared with the Ag-Bi alloy.

Similarly, the one (sample No. 54) obtained by adding Nd and Cu to the Ag-Sb alloy (sample No. 7), the one (sample No. 55) obtained by adding Nd and Au thereto, the one (sample No. 56) obtained by adding Y and Cu thereto, and the one (sample No. 57) obtained by adding Y and Au thereto have a still further improved durability as compared with the Ag-Sb alloy (sample No. 7).

[0062]

[Effect of the Invention]

The Ag base alloy reflective film or semi-transmissive reflective film for an optical information recording medium of the present invention has high thermal conductivity / high reflectance / high durability as described above, and hence it becomes possible to significantly enhance the recording and reproduction characteristics and the reliability of the optical information recording medium (particularly, a high speed DVD or a next-generation optical disk). Whereas, the Ag base alloy sputtering target for an optical information recording medium of the present invention is preferably used for the deposition of the foregoing reflective film or semi-transmissive reflective film. The reflective film or the semi-transmissive reflective film deposited using this is excellent in alloy composition, alloy element distribution, and in-plane uniformity of film thickness. In addition, the reflective film or the semi-transmissive reflective film has a low content of

impurity components, and hence it is favorably exploited to show high performances (high thermal conductivity, high reflectance, and high durability) as a reflective film, which allows the production of high-performance high-reliability optical information recording medium. Further, the optical information recording media having the reflective film and the semi-transmissive reflective film become capable of significantly enhance the recording and reproduction characteristics and the reliability.

[Name of the Document] ABSTRACT

[Abstract]

[Problem] To provide an Ag base alloy reflective film or semi-transmissive reflective film for an optical information recording medium, capable of imparting high reliability to a high-speed DVD or a next-generation optical disk, and an Ag base alloy sputtering target for an optical information recording medium to be used for deposition of the reflective film or the semi-transmissive reflective film, and an optical information recording medium having the reflective film or the semi-transmissive reflective film, by finding an Ag base alloy having higher thermal conductivity / higher reflectance / higher durability than those of pure Ag and conventional Ag alloys.

[Solving Means] An Ag base alloy containing Bi and/or Sb in a total amount of 0.005 to 0.4 % (denoting atomic %, the same goes for the following) is used.

[Table 1]
Results of thermal conductivity measurement

Sample No.	Composition	Thermal conductivity [W/(m·K)]	High thermal conductivity
1	Pure Ag	320	O
2	Ag-0.005at% Bi Alloy	319	O
3	Ag-0.2at% Bi Alloy	296	O
4	Ag-0.4at% Bi Alloy	271	O
5	Ag-0.6at% Bi Alloy	247	×
6	Ag-0.005at% Sb Alloy	319	O
7	Ag-0.2at% Sb Alloy	292	O
8	Ag-0.4at% Sb Alloy	264	O
9	Ag-0.6at% Sb Alloy	236	×
10	Ag-0.2at% Bi-0.01at% Nd Alloy	296	O
11	Ag-0.2at% Bi-0.1at% Nd Alloy	294	O
12	Ag-0.2at% Bi-0.5at% Nd Alloy	287	O
13	Ag-0.2at% Bi-2at% Nd Alloy	260	O
14	Ag-0.2at% Bi-3at% Nd Alloy	242	×
15	Ag-0.2at% Bi-0.01at% Y Alloy	296	O
16	Ag-0.2at% Bi-0.1at% Y Alloy	294	O
17	Ag-0.2at% Bi-0.5at% Y Alloy	288	O
18	Ag-0.2at% Bi-2at% Y Alloy	262	O
19	Ag-0.2at% Bi-3at% Y Alloy	245	×
20	Ag-0.2at% Sb-0.01at% Nd Alloy	292	O
21	Ag-0.2at% Sb-0.1at% Nd Alloy	290	O
22	Ag-0.2at% Sb-0.5at% Nd Alloy	283	O
23	Ag-0.2at% Sb-2at% Nd Alloy	256	O
24	Ag-0.2at% Sb-3at% Nd Alloy	238	×
25	Ag-0.2at% Sb-0.01at% Y Alloy	292	O
26	Ag-0.2at% Sb-0.1at% Y Alloy	290	O
27	Ag-0.2at% Sb-0.5at% Y Alloy	284	O
28	Ag-0.2at% Sb-2at% Y Alloy	258	O
29	Ag-0.2at% Sb-3at% Y Alloy	241	×

[Table 2]
Results of thermal conductivity measurement

Sample No.	Composition	Thermal conductivity [W/(m·K)]	High thermal conductivity
1	Pure Ag	320	○
30	Ag-0.2at% Bi-0.01at% Cu Alloy	296	○
31	Ag-0.2at% Bi-0.1at% Cu Alloy	295	○
32	Ag-0.2at% Bi-0.5at% Cu Alloy	290	○
33	Ag-0.2at% Bi-3at% Cu Alloy	260	○
34	Ag-0.2at% Bi-4at% Cu Alloy	248	×
35	Ag-0.2at% Bi-0.01at% Au Alloy	296	○
36	Ag-0.2at% Bi-0.1at% Au Alloy	295	○
37	Ag-0.2at% Bi-0.5at% Au Alloy	290	○
38	Ag-0.2at% Bi-3at% Au Alloy	262	○
39	Ag-0.2at% Bi-4at% Au Alloy	251	×
40	Ag-0.2at% Sb-0.01at% Cu Alloy	292	○
41	Ag-0.2at% Sb-0.1at% Cu Alloy	291	○
42	Ag-0.2at% Sb-0.5at% Cu Alloy	286	○
43	Ag-0.2at% Sb-3at% Cu Alloy	256	○
44	Ag-0.2at% Sb-4at% Cu Alloy	244	×
45	Ag-0.2at% Sb-0.01at% Au Alloy	292	○
46	Ag-0.2at% Sb-0.1at% Au Alloy	291	○
47	Ag-0.2at% Sb-0.5at% Au Alloy	286	○
48	Ag-0.2at% Sb-3at% Au Alloy	258	○
49	Ag-0.2at% Sb-4at% Au Alloy	247	×
50	Ag-0.2at% Bi-0.5at% Nd-0.5at% Cu Alloy	281	○
51	Ag-0.2at% Bi-0.5at% Nd-0.5at% Au Alloy	281	○
52	Ag-0.2at% Bi-0.5at% Y-0.5at% Cu Alloy	282	○
53	Ag-0.2at% Bi-0.5at% Y-0.5at% Au Alloy	282	○
54	Ag-0.2at% Sb-0.5at% Nd-0.5at% Cu Alloy	277	○
55	Ag-0.2at% Sb-0.5at% Nd-0.5at% Au Alloy	277	○
56	Ag-0.2at% Sb-0.5at% Y-0.5at% Cu Alloy	278	○
57	Ag-0.2at% Sb-0.5at% Y-0.5at% Au Alloy	278	○
58	Ag-0.2at% Si Alloy	265	○
59	Ag-0.2at% Sn Alloy	248	×

[Table 3]
Results of reflectance measurement

Sample No.	Composition	Reflectance relative to Pure Ag [%]		High reflectance
		Wavelength 405nm	Wavelength 650nm	
1	Pure Ag	90.8	92.5	○
2	Ag-0.005at% Bi Alloy	90.7	92.5	○
3	Ag-0.2at% Bi Alloy	86.2	90.8	○
4	Ag-0.4at% Bi Alloy	81.6	89.1	○
5	Ag-0.6at% Bi Alloy	77.0	87.4	×
6	Ag-0.005at% Sb Alloy	90.7	92.5	○
7	Ag-0.2at% Sb Alloy	86.1	90.7	○
8	Ag-0.4at% Sb Alloy	81.4	88.9	○
9	Ag-0.6at% Sb Alloy	76.7	87.1	×
10	Ag-0.2at% Bi-0.01at% Nd Alloy	86.2	90.8	○
11	Ag-0.2at% Bi-0.1at% Nd Alloy	85.9	90.7	○
12	Ag-0.2at% Bi-0.5at% Nd Alloy	84.8	90.3	○
13	Ag-0.2at% Bi-2at% Nd Alloy	80.7	88.6	○
14	Ag-0.2at% Bi-3at% Nd Alloy	78.0	87.5	×
15	Ag-0.2at% Bi-0.01at% Y Alloy	86.2	90.8	○
16	Ag-0.2at% Bi-0.1at% Y Alloy	85.9	90.7	○
17	Ag-0.2at% Bi-0.5at% Y Alloy	84.7	90.2	○
18	Ag-0.2at% Bi-2at% Y Alloy	80.3	88.4	○
19	Ag-0.2at% Bi-3at% Y Alloy	77.4	87.2	×
20	Ag-0.2at% Sb-0.01at% Nd Alloy	86.1	90.7	○
21	Ag-0.2at% Sb-0.1at% Nd Alloy	85.8	90.6	○
22	Ag-0.2at% Sb-0.5at% Nd Alloy	84.7	90.2	○
23	Ag-0.2at% Sb-2at% Nd Alloy	80.6	88.5	○
24	Ag-0.2at% Sb-3at% Nd Alloy	77.9	87.4	×
25	Ag-0.2at% Sb-0.01at% Y Alloy	86.1	90.7	○
26	Ag-0.2at% Sb-0.1at% Y Alloy	85.8	90.6	○
27	Ag-0.2at% Sb-0.5at% Y Alloy	84.6	90.1	○
28	Ag-0.2at% Sb-2at% Y Alloy	80.2	88.3	○
29	Ag-0.2at% Sb-3at% Y Alloy	77.3	87.1	×

[Table 4]
Results of reflectance measurement

Sample No.	Composition	Reflectance relative to Pure Ag [%]		High reflectance
		Wavelength 405nm	Wavelength 650nm	
1	Pure Ag	90.8	92.5	○
30	Ag-0.2at% Bi-0.01at% Cu Alloy	86.2	90.8	○
31	Ag-0.2at% Bi-0.1at% Cu Alloy	86.0	90.7	○
32	Ag-0.2at% Bi-0.5at% Cu Alloy	85.3	90.4	○
33	Ag-0.2at% Bi-3at% Cu Alloy	81.0	88.3	○
34	Ag-0.2at% Bi-4at% Cu Alloy	79.3	87.5	×
35	Ag-0.2at% Bi-0.01at% Au Alloy	86.2	90.8	○
36	Ag-0.2at% Bi-0.1at% Au Alloy	86.0	90.7	○
37	Ag-0.2at% Bi-0.5at% Au Alloy	85.4	90.4	○
38	Ag-0.2at% Bi-3at% Au Alloy	81.5	88.5	○
39	Ag-0.2at% Bi-4at% Au Alloy	79.9	87.7	×
40	Ag-0.2at% Sb-0.01at% Cu Alloy	86.1	90.7	○
41	Ag-0.2at% Sb-0.1at% Cu Alloy	85.9	90.6	○
42	Ag-0.2at% Sb-0.5at% Cu Alloy	85.2	90.3	○
43	Ag-0.2at% Sb-3at% Cu Alloy	80.9	88.2	○
44	Ag-0.2at% Sb-4at% Cu Alloy	79.2	87.4	×
45	Ag-0.2at% Sb-0.01at% Au Alloy	86.1	90.7	○
46	Ag-0.2at% Sb-0.1at% Au Alloy	85.9	90.6	○
47	Ag-0.2at% Sb-0.5at% Au Alloy	85.3	90.3	○
48	Ag-0.2at% Sb-3at% Au Alloy	81.4	88.4	○
49	Ag-0.2at% Sb-4at% Au Alloy	79.8	87.6	×
50	Ag-0.2at% Bi-0.5at% Nd-0.5at% Cu Alloy	84.0	89.8	○
51	Ag-0.2at% Bi-0.5at% Nd-0.5at% Au Alloy	84.0	89.9	○
52	Ag-0.2at% Bi-0.5at% Y-0.5at% Cu Alloy	83.9	89.8	○
53	Ag-0.2at% Bi-0.5at% Y-0.5at% Au Alloy	83.9	89.8	○
54	Ag-0.2at% Sb-0.5at% Nd-0.5at% Cu Alloy	83.9	89.7	○
55	Ag-0.2at% Sb-0.5at% Nd-0.5at% Au Alloy	83.9	89.8	○
56	Ag-0.2at% Sb-0.5at% Y-0.5at% Cu Alloy	83.8	89.7	○
57	Ag-0.2at% Sb-0.5at% Y-0.5at% Au Alloy	83.8	89.7	○
58	Ag-0.2at% Si Alloy	85.5	90.3	○
59	Ag-0.2at% Sn Alloy	85.0	89.9	○

[Table 5]
Results of durability (thermal stability) evaluation

Sample No.	Composition	Change in reflectance before and after high temperature high humidity test [%]		High durability
		Wavelength 405nm	Wavelength 650nm	
1	Pure Ag	-27.3	-3.0	×
2	Ag-0.005at% Bi Alloy	-1.4	-0.8	○
3	Ag-0.2at% Bi Alloy	-0.7	-0.3	○
4	Ag-0.4at% Bi Alloy	-0.5	-0.2	○
5	Ag-0.6at% Bi Alloy	-0.3	-0.1	○
6	Ag-0.005at% Sb Alloy	-1.6	-0.9	○
7	Ag-0.2at% Sb Alloy	-0.8	-0.4	○
8	Ag-0.4at% Sb Alloy	-0.6	-0.3	○
9	Ag-0.6at% Sb Alloy	-0.4	-0.2	○
10	Ag-0.2at% Bi-0.01at% Nd Alloy	-0.6	-0.2	○
11	Ag-0.2at% Bi-0.1at% Nd Alloy	-0.5	-0.1	○
12	Ag-0.2at% Bi-0.5at% Nd Alloy	-0.3	-0.1	○
13	Ag-0.2at% Bi-2at% Nd Alloy	0.0	0.0	○
14	Ag-0.2at% Bi-3at% Nd Alloy	0.0	0.0	○
15	Ag-0.2at% Bi-0.01at% Y Alloy	-0.6	-0.2	○
16	Ag-0.2at% Bi-0.1at% Y Alloy	-0.5	-0.1	○
17	Ag-0.2at% Bi-0.5at% Y Alloy	-0.4	-0.1	○
18	Ag-0.2at% Bi-2at% Y Alloy	0.0	0.0	○
19	Ag-0.2at% Bi-3at% Y Alloy	0.0	0.0	○
20	Ag-0.2at% Sb-0.01at% Nd Alloy	-0.7	-0.3	○
21	Ag-0.2at% Sb-0.1at% Nd Alloy	-0.6	-0.2	○
22	Ag-0.2at% Sb-0.5at% Nd Alloy	-0.4	-0.2	○
23	Ag-0.2at% Sb-2at% Nd Alloy	0.0	0.0	○
24	Ag-0.2at% Sb-3at% Nd Alloy	0.0	0.0	○
25	Ag-0.2at% Sb-0.01at% Y Alloy	-0.7	-0.3	○
26	Ag-0.2at% Sb-0.1at% Y Alloy	-0.6	-0.2	○
27	Ag-0.2at% Sb-0.5at% Y Alloy	-0.5	-0.2	○
28	Ag-0.2at% Sb-2at% Y Alloy	0.0	0.0	○
29	Ag-0.2at% Sb-3at% Y Alloy	0.0	0.0	○

[Table 6]
Results of durability (thermal stability) evaluation

Sample No.	Composition	Change in reflectance before and after high temperature high humidity test [%]		High durability
		Wavelength 405nm	Wavelength 650nm	
1	Pure Ag	-27.3	-3.0	×
30	Ag-0.2at% Bi-0.01at% Cu Alloy	-0.6	-0.2	O
31	Ag-0.2at% Bi-0.1at% Cu Alloy	-0.5	-0.1	O
32	Ag-0.2at% Bi-0.5at% Cu Alloy	-0.4	-0.1	O
33	Ag-0.2at% Bi-3at% Cu Alloy	0.0	0.0	O
34	Ag-0.2at% Bi-4at% Cu Alloy	0.0	0.0	O
35	Ag-0.2at% Bi-0.01at% Au Alloy	-0.6	-0.2	O
36	Ag-0.2at% Bi-0.1at% Au Alloy	-0.5	-0.1	O
37	Ag-0.2at% Bi-0.5at% Au Alloy	-0.4	-0.1	O
38	Ag-0.2at% Bi-3at% Au Alloy	0.0	0.0	O
39	Ag-0.2at% Bi-4at% Au Alloy	0.0	0.0	O
40	Ag-0.2at% Sb-0.01at% Cu Alloy	-0.7	-0.3	O
41	Ag-0.2at% Sb-0.1at% Cu Alloy	-0.6	-0.2	O
42	Ag-0.2at% Sb-0.5at% Cu Alloy	-0.4	-0.1	O
43	Ag-0.2at% Sb-3at% Cu Alloy	0.0	0.0	O
44	Ag-0.2at% Sb-4at% Cu Alloy	0.0	0.0	O
45	Ag-0.2at% Sb-0.01at% Au Alloy	-0.7	-0.3	O
46	Ag-0.2at% Sb-0.1at% Au Alloy	-0.5	-0.2	O
47	Ag-0.2at% Sb-0.5at% Au Alloy	-0.3	-0.1	O
48	Ag-0.2at% Sb-3at% Au Alloy	0.0	0.0	O
49	Ag-0.2at% Sb-4at% Au Alloy	0.0	0.0	O
50	Ag-0.2at% Bi-0.5at% Nd-0.5at% Cu Alloy	0.0	0.0	O
51	Ag-0.2at% Bi-0.5at% Nd-0.5at% Au Alloy	0.0	0.0	O
52	Ag-0.2at% Bi-0.5at% Y-0.5at% Cu Alloy	0.0	0.0	O
53	Ag-0.2at% Bi-0.5at% Y-0.5at% Au Alloy	0.0	0.0	O
54	Ag-0.2at% Sb-0.5at% Nd-0.5at% Cu Alloy	0.0	0.0	O
55	Ag-0.2at% Sb-0.5at% Nd-0.5at% Au Alloy	0.0	0.0	O
56	Ag-0.2at% Sb-0.5at% Y-0.5at% Cu Alloy	0.0	0.0	O
57	Ag-0.2at% Sb-0.5at% Y-0.5at% Au Alloy	0.0	0.0	O
58	Ag-0.2at% Si Alloy	-19.9	-2.1	×
59	Ag-0.2at% Sn Alloy	-18.4	-1.8	×

[Table 7]
Change in appearance after salt immersion test of Ag-based thin film

Sample No.	Composition	Change in appearance after salt immersion test	High durability
1	Pure Ag	Yes	×
2	Ag-0.005at% Bi Alloy	No	○
3	Ag-0.2at% Bi Alloy	No	○
4	Ag-0.4at% Bi Alloy	No	○
5	Ag-0.6at% Bi Alloy	No	○
6	Ag-0.005at% Sb Alloy	No	○
7	Ag-0.2at% Sb Alloy	No	○
8	Ag-0.4at% Sb Alloy	No	○
9	Ag-0.6at% Sb Alloy	No	○
10	Ag-0.2at% Bi-0.01at% Nd Alloy	No	○
11	Ag-0.2at% Bi-0.1at% Nd Alloy	No	○
12	Ag-0.2at% Bi-0.5at% Nd Alloy	No	○
13	Ag-0.2at% Bi-2at% Nd Alloy	No	○
14	Ag-0.2at% Bi-3at% Nd Alloy	No	○
15	Ag-0.2at% Bi-0.01at% Y Alloy	No	○
16	Ag-0.2at% Bi-0.1at% Y Alloy	No	○
17	Ag-0.2at% Bi-0.5at% Y Alloy	No	○
18	Ag-0.2at% Bi-2at% Y Alloy	No	○
19	Ag-0.2at% Bi-3at% Y Alloy	No	○
20	Ag-0.2at% Sb-0.01at% Nd Alloy	No	○
21	Ag-0.2at% Sb-0.1at% Nd Alloy	No	○
22	Ag-0.2at% Sb-0.5at% Nd Alloy	No	○
23	Ag-0.2at% Sb-2at% Nd Alloy	No	○
24	Ag-0.2at% Sb-3at% Nd Alloy	No	○
25	Ag-0.2at% Sb-0.01at% Y Alloy	No	○
26	Ag-0.2at% Sb-0.1at% Y Alloy	No	○
27	Ag-0.2at% Sb-0.5at% Y Alloy	No	○
28	Ag-0.2at% Sb-2at% Y Alloy	No	○
29	Ag-0.2at% Sb-3at% Y Alloy	No	○

[Table 8]
Change in appearance after salt immersion test of Ag-based thin film

Sample No.	Composition	Change in appearance after salt immersion test	High durability
1	Pure Ag	Yes	×
30	Ag-0.2at% Bi-0.01at% Cu Alloy	No	○
31	Ag-0.2at% Bi-0.1at% Cu Alloy	No	○
32	Ag-0.2at% Bi-0.5at% Cu Alloy	No	○
33	Ag-0.2at% Bi-3at% Cu Alloy	No	○
34	Ag-0.2at% Bi-4at% Cu Alloy	No	○
35	Ag-0.2at% Bi-0.01at% Au Alloy	No	○
36	Ag-0.2at% Bi-0.1at% Au Alloy	No	○
37	Ag-0.2at% Bi-0.5at% Au Alloy	No	○
38	Ag-0.2at% Bi-3at% Au Alloy	No	○
39	Ag-0.2at% Bi-4at% Au Alloy	No	○
40	Ag-0.2at% Sb-0.01at% Cu Alloy	No	○
41	Ag-0.2at% Sb-0.1at% Cu Alloy	No	○
42	Ag-0.2at% Sb-0.5at% Cu Alloy	No	○
43	Ag-0.2at% Sb-3at% Cu Alloy	No	○
44	Ag-0.2at% Sb-4at% Cu Alloy	No	○
45	Ag-0.2at% Sb-0.01at% Au Alloy	No	○
46	Ag-0.2at% Sb-0.1at% Au Alloy	No	○
47	Ag-0.2at% Sb-0.5at% Au Alloy	No	○
48	Ag-0.2at% Sb-3at% Au Alloy	No	○
49	Ag-0.2at% Sb-4at% Au Alloy	No	○
50	Ag-0.2at% Bi-0.5at% Nd-0.5at% Cu Alloy	No	○
51	Ag-0.2at% Bi-0.5at% Nd-0.5at% Au Alloy	No	○
52	Ag-0.2at% Bi-0.5at% Y-0.5at% Cu Alloy	No	○
53	Ag-0.2at% Bi-0.5at% Y-0.5at% Au Alloy	No	○
54	Ag-0.2at% Sb-0.5at% Nd-0.5at% Cu Alloy	No	○
55	Ag-0.2at% Sb-0.5at% Nd-0.5at% Au Alloy	No	○
56	Ag-0.2at% Sb-0.5at% Y-0.5at% Cu Alloy	No	○
57	Ag-0.2at% Sb-0.5at% Y-0.5at% Au Alloy	No	○
58	Ag-0.2at% Si Alloy	Yes	×
59	Ag-0.2at% Sn Alloy	Yes	×

[Table 9]
Average roughness before and after high temperature high humidity test of Ag-based thin film

Sample No.	Composition	Average roughness before and after high temperature high humidity test [nm]		High durability
		Before test	After test	
1	Pure Ag	4.18	7.33	×
2	Ag-0.005at% Bi Alloy	0.63	0.93	○
3	Ag-0.2at% Bi Alloy	0.58	0.61	○
4	Ag-0.4at% Bi Alloy	0.55	0.58	○
5	Ag-0.6at% Bi Alloy	0.52	0.54	○
6	Ag-0.005at% Sb Alloy	0.65	0.95	○
7	Ag-0.2at% Sb Alloy	0.58	0.63	○
8	Ag-0.4at% Sb Alloy	0.56	0.59	○
9	Ag-0.6at% Sb Alloy	0.54	0.57	○
10	Ag-0.2at% Bi-0.01at% Nd Alloy	0.58	0.60	○
11	Ag-0.2at% Bi-0.1at% Nd Alloy	0.55	0.59	○
12	Ag-0.2at% Bi-0.5at% Nd Alloy	0.52	0.56	○
13	Ag-0.2at% Bi-2at% Nd Alloy	0.45	0.48	○
14	Ag-0.2at% Bi-3at% Nd Alloy	0.44	0.48	○
15	Ag-0.2at% Bi-0.01at% Y Alloy	0.57	0.60	○
16	Ag-0.2at% Bi-0.1at% Y Alloy	0.56	0.59	○
17	Ag-0.2at% Bi-0.5at% Y Alloy	0.53	0.58	○
18	Ag-0.2at% Bi-2at% Y Alloy	0.47	0.53	○
19	Ag-0.2at% Bi-3at% Y Alloy	0.45	0.52	○
20	Ag-0.2at% Sb-0.01at% Nd Alloy	0.58	0.62	○
21	Ag-0.2at% Sb-0.1at% Nd Alloy	0.56	0.60	○
22	Ag-0.2at% Sb-0.5at% Nd Alloy	0.53	0.58	○
23	Ag-0.2at% Sb-2at% Nd Alloy	0.47	0.50	○
24	Ag-0.2at% Sb-3at% Nd Alloy	0.47	0.49	○
25	Ag-0.2at% Sb-0.01at% Y Alloy	0.58	0.63	○
26	Ag-0.2at% Sb-0.1at% Y Alloy	0.55	0.61	○
27	Ag-0.2at% Sb-0.5at% Y Alloy	0.54	0.60	○
28	Ag-0.2at% Sb-2at% Y Alloy	0.46	0.54	○
29	Ag-0.2at% Sb-3at% Y Alloy	0.45	0.53	○

[Table 10]

Average roughness before and after high temperature high humidity test of Ag-based thin film

Sample No.	Composition	Average roughness before and after high temperature high humidity test [nm]		High durability
		Before test	After test	
1	Pure Ag	4.18	7.33	×
30	Ag-0.2at% Bi-0.01at% Cu Alloy	0.59	0.93	○
31	Ag-0.2at% Bi-0.1at% Cu Alloy	0.58	0.90	○
32	Ag-0.2at% Bi-0.5at% Cu Alloy	0.56	0.86	○
33	Ag-0.2at% Bi-3at% Cu Alloy	0.55	0.75	○
34	Ag-0.2at% Bi-4at% Cu Alloy	0.54	0.73	○
35	Ag-0.2at% Bi-0.01at% Au Alloy	0.59	0.94	○
36	Ag-0.2at% Bi-0.1at% Au Alloy	0.57	0.89	○
37	Ag-0.2at% Bi-0.5at% Au Alloy	0.56	0.84	○
38	Ag-0.2at% Bi-3at% Au Alloy	0.54	0.76	○
39	Ag-0.2at% Bi-4at% Au Alloy	0.53	0.75	○
40	Ag-0.2at% Sb-0.01at% Cu Alloy	0.59	0.95	○
41	Ag-0.2at% Sb-0.1at% Cu Alloy	0.58	0.91	○
42	Ag-0.2at% Sb-0.5at% Cu Alloy	0.57	0.88	○
43	Ag-0.2at% Sb-3at% Cu Alloy	0.56	0.78	○
44	Ag-0.2at% Sb-4at% Cu Alloy	0.54	0.77	○
45	Ag-0.2at% Sb-0.01at% Au Alloy	0.58	0.94	○
46	Ag-0.2at% Sb-0.1at% Au Alloy	0.58	0.90	○
47	Ag-0.2at% Sb-0.5at% Au Alloy	0.57	0.86	○
48	Ag-0.2at% Sb-3at% Au Alloy	0.57	0.79	○
49	Ag-0.2at% Sb-4at% Au Alloy	0.55	0.77	○
50	Ag-0.2at% Bi-0.5at% Nd-0.5at% Cu Alloy	0.50	0.55	○
51	Ag-0.2at% Bi-0.5at% Nd-0.5at% Au Alloy	0.51	0.56	○
52	Ag-0.2at% Bi-0.5at% Y-0.5at% Cu Alloy	0.52	0.57	○
53	Ag-0.2at% Bi-0.5at% Y-0.5at% Au Alloy	0.51	0.55	○
54	Ag-0.2at% Sb-0.5at% Nd-0.5at% Cu Alloy	0.52	0.58	○
55	Ag-0.2at% Sb-0.5at% Nd-0.5at% Au Alloy	0.53	0.60	○
56	Ag-0.2at% Sb-0.5at% Y-0.5at% Cu Alloy	0.52	0.59	○
57	Ag-0.2at% Sb-0.5at% Y-0.5at% Au Alloy	0.54	0.59	○
58	Ag-0.2at% Si Alloy	0.68	1.17	×
59	Ag-0.2at% Sn Alloy	0.79	1.25	×